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(19)

(54) FLAME-RETARDANT MELAMINE RESIN FIBRES AND A METHOD OF MANUFACTURING THE SAME

5 (71) We, KURARAY CO., LTD., a Japanese Company of 1621, Sakazu, Kurashiki-City, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention concerns amino-triazine resin fibers and a process for their preparation.

15 The need for flame-retardant fibers is critical in certain applications. Recently, however, with a view toward preventing fire and related disasters, it has been desirable that even ordinary textile products for general use, such as clothing, bedding, curtains, matting and carpets, should have flame-retardant properties. There has been a recent awareness concerning flame-retardancy in textile goods. For example, children's clothing has been criticised recently for not affording the best protection against fire to the child, and therefore the need for flame-retardant clothing has increased in recent times.

20 If non-flame-retardant textile goods are exposed to fire, the flames will be propagated rapidly which may result not only in heavy property but also bodily injury or even death. Therefore, to prevent fires and related accidents, the demand for non-combustible or flame-retardant textile fibers has increased in recent times.

In addition to possessing flame-retardant properties, it is also desirable that textiles and fibers be thermally infusible and have low thermal shrinkage. If textile goods are thermally fusible or highly thermally shrinkable, and are exposed to fire, the flames may spread through them extremely rapidly in view of the spaces or "holes" in the textile goods caused by fusion or shrinkage near the fire, which may possibly result in bodily injury if, for example, the article is a piece of clothing. Moreover, the wearer of such clothing may be burned by contact with the molten polymer of which the clothing is constituted, or the hot contracted fibers thereof. Accordingly, the infusibility and shrinkability of the fibers are considered to be important safety factors especially in clothing apparel.

35 Furthermore, from the standpoint of preventing disasters in a fire, it is desirable that such textile goods should generate as small an amount of smoke or poisonous gas as possible when heated, since, if large amounts of smoke and/or poisonous gas are generated when the textile article is heated, there is the high probability that rapid escape from the fire will be impossible, and, more significantly, there is a danger of suffocation in such circumstances, particularly in a closed area such as a home.

40 Almost all well-known fibers in general use are extremely inflammable and therefore

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dangerous. Exceptions are special fibers such as inorganic fibers, carbon fibers and phenol resin fibers. Even if a fiber is flame-retardant, it is normally fusible or thermally shrinkable, or it may generate large quantities of smoke and/or poisonous gas when heated. Thus, given these properties, even if a fiber is flame-retardant, the fiber would be deficient in preventing fire damage and possible bodily injury. In other words, in addition to flame retardancy *per se*, it is often absolutely necessary that a fiber should have the above properties as well.

The above special fibers, despite their flame-retardant properties, are yet undesirable for general use in the textile field. Thus, although inorganic and carbon fibers have desirable flame-retardant properties, they are not generally used in forming textile goods in view of their many defects in properties necessary for such general use. Specifically, such fibers have very poor spinnability and weavability due to their low strength and flexibility, and they have a large thermal conductivity, a low hygroscopicity, poor handle and low dyeability. Moreover, although phenol resin fibers have been attracting attention for their flame-retardant properties, it is difficult to spin and weave such fibers in view of their low strength, as they exhibit tenacities of only 1—1.5 g/d. Further, phenol resin fibers have a characteristic yellow-brown color and are quickly colored by the sun even after being bleached almost white. Further, they have a poor dyeability. Such properties are totally unacceptable in textile fibers for general usage, and therefore phenol resin fibers have not been broadly used in the textile field.

There is an obvious need, therefore, for fibers which, besides being flame-retardant, have the other properties required for general use in textile goods.

The present invention provides a flame-retardant and thermally infusible textile fiber comprising at least 60 weight per cent of a cured aminotriazine-aldehyde resin, having a degree of water swelling below 2.0.

The degree of swelling as applied to any particular solvent is defined as W/W_0 , where W is the weight of the fiber determined after immersing the dry fiber in a solvent for a fixed period of time and W_0 is the weight of the same absolute dry fiber.

The present invention also provides a process for the production of such fibers, comprising spinning a solvent solution of an aminotriazine-aldehyde pre-condensate into a heated atmosphere to simultaneously effect evaporation of the solution solvent and curing of the pre-condensate continuously until the desired degree of water-swelling is achieved.

There is no prior disclosure that fibers can be made consisting predominantly of melamine-aldehyde resins. Japanese Patent Publication No. 47—14771 (Register No. 665688 pub-

lished in 1972) discloses fibers produced from a mixture of polyvinyl alcohol (hereinafter "PVA") and an N-methylol aminotriazine or methylated N-methylol aminotriazine. However, the mixture is disclosed as containing from 5 to 20 weight percent, based on the weight of the PVA, of the resin. In contradistinction, the fibers produced by the process of the present invention, the minimum amount of aminotriazine aldehyde resin present in the fibers is at least 60 weight percent, preferably at least 70 weight per cent, of the fiber. The process disclosed in this Japanese patent is essentially a dry spinning process used to produce PVA fibers. In addition, the fibers obtained by this process have substantially the same properties as PVA fibers, since they burn on contact with a flame and are completely fused and exhibit a large thermal shrinkage, since they fuse at 300° C. Fibers produced by the process of the present invention are flame-retardant and infusible and exhibit an extremely low thermal shrinkage when heated. Accordingly, the process of the present invention is fundamentally different from the process disclosed in said Japanese patent, as are the two fibers produced by the respective processes.

Moreover, an aminotriazine-formaldehyde resin has often been used in a finishing treatment for coating textiles or fabrics. In this case, only a small amount of aminotriazine resin exists adhered on the surface of the fibers constituting the fabrics and such fibers coated with a melamine resin are completely different from the fibers of the present invention which are actually formed of aminotriazine-aldehyde resins.

More specifically, in one embodiment the fibers of the present invention consist essentially of 100% by weight of the aminotriazine-aldehyde resins described below. Of course, minor amounts of impurities may be present in these resins derived, possibly from the process used for preparing the same. In another embodiment according to the present invention, the fibers comprise aminotriazine-aldehyde resins condensed or mixed with other fiber-forming polymers. It is required, however, that fibers of this embodiment contain at least 60 weight percent, preferably 70 weight percent, of the aminotriazine-aldehyde resins described below, based on the entire weight of the fiber. Thus, the fibers of the present invention are to be distinguished from fibers which contain minor amounts of aminotriazine-aldehyde resins or which are coated with such resins.

The aminotriazine-aldehyde pre-condensates used to form the fibers of the present invention are soluble (in water and organic solvents) and thermally fusible low molecular weight resins obtained by the reaction of an aminotriazine with an aldehyde by any conventional

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process. See, for example, Vale and Taylor "Aminoplastics", 1964, P-44 and Walker "Formaldehyde", 1944, P-218.

Alternatively, certain such aminotriazine-aldehyde pre-condensates are available commercially and such products may be used in the present invention.

The conditions of reaction between the aminotriazine or mixture of aminotriazines and the aldehyde or mixture of aldehydes to form such pre-condensates are not particularly critical. Generally, the reaction may be conducted within a temperature range of 50 to 90° C for a period of time of from 10 min. to 3 hrs. The pH of the reaction mixture is preferably within the range of 5 to 9, but the reaction may also be conducted under neutral or weakly acidic conditions.

The reaction may be conducted in a solvent for one or both reactants, but the particular solvent utilized is not critical, with any material that is a solvent for one or both reactants being operable in this process. The preferred solvent is water, and in addition other solvents such as organic solvents can be used. Typical organic solvents include alcohols, acetone, dimethyl formamide, dimethyl sulfoxide, dimethyl acetamide, phenols and mixtures thereof.

In addition, the reaction may be conducted in the presence of either acidic or alkaline catalyst. Typical acidic catalysts include hydrochloric acid, sulfuric acid, formic acid, acetic acid and oxalic acid, and typical alkaline catalysts are sodium hydroxide, potassium hydroxide, sodium carbonate and sodium bicarbonate.

The ratio of the reactants is also not particularly critical. Taking the reaction between 2,4,6-tri-amino-s-triazine (hereinafter sometimes referred to as "melamine") and formaldehyde as an example, it is possible to react one mole of melamine with up to 6 moles of the formaldehyde (due to the presence of the 3 amino groups in the triazine compound). The reaction product is said to have a degree of methylolation or hydroxymethylation of 6 when one mole of the melamine is bonded to 6 moles of the formaldehyde. The degree of hydroxymethylation can be determined by, for example, measuring the difference in amount between the formaldehyde added to the reaction system and the unreacted formaldehyde remaining after reaction, relative to the amount of melamine. The fibers produced by the process of the present invention can be prepared from pre-condensates having a degree of hydroxymethylation of from 1.5 to 6.0. Preferably, however, from the viewpoint of flame-retardancy and mechanical properties of the fibers, the degree of hydroxymethylation in the pre-condensate should be from 2.0 to 6.0.

The above reaction conditions between the melamine and the aldehyde may be varied

depending upon the results desired, and with the preferred conditions in mind. The reaction per se may be effected in conventional manner and therefore any modifications involved will be familiar.

It is preferred that the reaction be conducted in a solvent, preferably water. The pre-condensate formed by the reaction may be recovered as a powder by subjecting the reaction product solution to successive operations of concentration, cooling, addition of a precipitation agent and drying. The product powder may then be dissolved in a solvent such as water to obtain the spinning solution used in the process of the present invention. Alternatively, the reaction product solution may be used directly as the spinning solution, with or without concentration or dilution to the desired concentration. Either alternative is possible to prepare the spinning solution used in the process of the present invention. A further alternative is that commercially available melamine-aldehyde pre-condensates in the form of a powder or aqueous solutions thereof may also be used.

An example of a process for preparing the melamine-aldehyde pre-condensate is as follows: N-methylol melamine (i.e., N-methylol-2,4,6-tri-amino-s-triazine) is produced by reacting melamine with formaldehyde. Reactions of other aminotriazines with other aldehydes may be effected in much the same manner. Into a reaction vessel are charged 1 mole of the melamine and 3 moles of formaldehyde (in the form of a 37 weight percent aqueous solution) and the pH of the resulting mixture is adjusted to 8-9 with an alkali such as caustic soda, sodium carbonate or sodium bicarbonate. The reaction is conducted by heating to a temperature of 75-85° C. for 60 min. The result is a pre-condensate of N-methylol melamine having a degree of hydroxymethylation of 2.7 and present in the form of an aqueous solution having a concentration of 56 weight percent.

The aminotriazines and aldehydes used in the present invention may be any of various types. Generally, the aminotriazine is 2,4,6-tri-amino-s-triazine, an N-substituted derivative thereof, guanamine or a substituted guanamine. The substituted derivative of said triazine may be a N- or N,N- or N,N,N-substituted triazine, with the particular substituent(s) not being critical, as long as the compound selected is capable of reacting with an aldehyde to form the pre-condensate used in the process of the present invention. Typical substituents include alkyl of 1 to 8 carbon atoms, allyl, aryl or 6 to 10 carbon atoms, and halogen-substituted alkyl of 1 to 8 carbon atoms.

Specific examples of N-substituted triazine derivatives are N - butyl - 2,4,6 - triamino-s - triazine; N,N - diallyl - 2,4,6 - triamino-s - triazine; N - *tert* - octyl - 2,4,6 - triamino-

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- s - triazine; and N - trihalogenomethyl-2,4,6-triamino-s-triazine.
- Examples of substituted guanamines are diguanamine, acetoguanamine and benzoguanamine.
- Mixtures of the above types of aminotriazine compounds may also be used in the present invention.
- The aldehyde used to form the pre-condensate is not particularly limited and broadly, the present invention includes any aldehyde capable of reacting with an aminotriazine to form the pre-condensate, which can be converted into a fiber by a spinning operation.
- Typical aldehydes include aliphatic (saturated and unsaturated), cyclic and aromatic aldehydes, and substituted derivatives thereof. Typical aliphatic aldehydes operable in the present invention include formaldehyde, acrolein, methylal, glyoxal, acetoaldehyde, polyoxymethylene, polyoxymethylene glycol and paraformaldehyde.
- Examples of cyclic aldehydes and aldehyde sources include paraformaldehyde, dioxolane, trioxane and tetraoxane.
- Examples of aromatic aldehydes include benzaldehyde, 2,4,6-trimethyl benzaldehyde and 1,2-diformylbenzene.
- Substituted derivatives of any of these aldehydes can be used in the present invention, typical substituents including hydroxy groups, amino groups and halogen atoms.
- Examples of substituted aldehydes include glycolic aldehyde, aminoacetaldehyde and chloral.
- Mixtures of the above aldehydes can also be used employed in the present invention.
- The preferred reactants are 2,4,6-triamino-s-triazine and formaldehyde. Broadly stated, the pre-condensate used in the process of the present invention is the condensation product of an aminotriazine and an aldehyde capable of being condensed together to form a compound of low molecular weight, which is thermally fusible and soluble in water and organic solvents, and that has a degree of hydroxymethylation of 1.5 to 6.0.
- The spinning solution of the present invention can be prepared from:
- (1) 100% aminotriazine-aldehyde condensation product, hereinafter referred to as "MACP";
 - (2) at least 60% by weight, based on the fiber weight, of MACP co-condensed with a compound capable of being condensed therewith and which does not decrease the flame-retardant and good fiber properties of the fiber of the present invention. Examples of such compounds are other aldehydes than that used in the MACP (such as acetaldehyde, acrolein, benzaldehyde and 2,4,6-trimethyl benzaldehyde), other aminotriazines than that used in the MACP (e.g. benzoguanamine, acetoguanamine, etc.) and other compounds such as phenol, cresol, urea, methylamine and ethylenediamine; and
 - (3) the product of condensation, or physical mixtures, of at least 60 weight percent (based on the weight of said product of condensation or mixture) of MACP and other fiber-forming natural or synthetic resins. Included within these "other resins" are thermosetting and thermoplastic resins, with water-soluble thermoplastic polymers being preferred. Polyvinyl alcohol (PVA) is preferred in amounts of from 5 to 40 weight percent, based on the fiber weight. Examples of suitable fiber-forming thermosetting resins are synthetic resins such as urea-formaldehyde resin, phenol-formaldehyde resin and epoxy resin.
 - Examples of suitable fiber-forming thermoplastic resins are water-soluble polymers, e.g. cellulose derivatives and polyvinyl-alcohol, and organic-solvent-soluble polymers, e.g. polyvinyl formal, polyvinylbutyral, polyamide, polyvinyl chloride, polyethyleneterephthalate and poly acrylonitrile.
 - The preferred water-soluble thermoplastic polymers include any such polymers that are fiber-forming and compatible with the MACP. Examples are cellulose derivatives (e.g. carboxymethyl cellulose, methyl cellulose and ethyl cellulose), polyacrylic acid, polyacrylamide, PVA (the preferred), polyvinyl pyrrolidone and polyethylene oxide.
 - alkyl ethers of the aminotriazine aldehyde condensation product formed by reacting the aminotriazine-aldehyde condensation product with, for example, alcohols to form alkylated methylol aminotriazines. An example is methylated methylol - 2,4,6 - triamino-s-triazine, which is obtained by reacting N-methylol melamine with methanol in the presence of an acid catalyst. Various alcohols may be used to form these alkylated derivatives, with monohydric primary alcohols being preferred, particularly C₁₋₄ monohydric primary alcohols such as methanol. These alkylated derivatives are generally prepared by reacting (with or without a catalyst) the aminotriazine-aldehyde condensation product with the alcohol at a temperature of from 60 to 80° C for 10 to 60 min.;
 - mixtures of the aminotriazine-aldehyde condensation product with fiber-forming natural or synthetic resins. Typical resins are thermosetting resins (other than aminotriazine-aldehyde resins) and thermoplastic resins, and mixtures thereof. Water-soluble thermoplastic fiber-forming resins are preferred, especially PVA; and
 - mixtures of any of the above types.
- Any of the above types of materials can be used to form the spinning solution of the present invention, any they will be referred to hereinafter collectively as the "pre-condensate".
- In those types of pre-condensates involving

- the presence of a material other than the aminotriazine-aldehyde condensation product per se, at least 60% by weight of the pre-condensate must comprise the aminotriazine-aldehyde condensation product. For example, in types (3) and (5), the aminotriazine-aldehyde condensation product must be present in an amount of at least 60% by weight, based on the weight of the entire pre-condensate. Preferably, at least 70% by weight of the aminotriazine-aldehyde condensation product is present in the pre-condensate. The minimum 60% by weight limitation is due to the fact that if the amount of melamine-aldehyde condensation product in the pre-condensate is less than this value, the properties of the fibers become inferior. For example, the specific properties attributed to the aminotriazine-aldehyde condensation product, such as flame-retardancy, may be reduced. In addition, the mechanical properties such as strength and elongation may also be reduced.
- Accordingly, any of the above materials may be used to form the spinning solution of the present invention. As pointed out above, the pre-condensate may be recovered as a powder from the reaction used to produce it, or the reaction solution may be used as such as the spinning solution with any necessary concentration and/or dilution, or the aminotriazine-aldehyde condensation product, which forms a part of the pre-condensate, may be obtained commercially. Regardless of the manner in which the pre-condensate is obtained, the spinning solution should have a pre-condensate concentration of from 20 to 85% by weight, based on the weight of the spinning solution. The spinning solution must be spinnable and stable; this is the reason for the preferred 20—85% concentration range.
- The preferred solvent for the spinning solution is water, and in addition other solvents such as organic solvents can be used. Typical organic solvents include alcohols, acetone, dimethyl formamide, dimethyl sulfoxide, dimethyl acetamide and phenols, and mixtures of such solvents.
- Generally, the spinnability of the solution depends upon its viscosity, although certain influences are exerted by the particular solvent used, the pH and aging temperature of the solution and the kinds and amount of additives that the solution contains. Good spinnability is exhibited when the viscosity, determined by using a B-type rotation viscosimeter, is within the range 40—3600 poises, at 35° C. When the pre-condensate concentration in the spinning solution is less than 20% by weight, it is difficult to obtain a viscosity of 40 poises, and if this viscosity cannot be obtained, spinnability is poor and a stable spinning process may be impossible. On the other hand, with a pre-condensate concentration of greater than 85% in the spinning solution, it is likely that its viscosity would be higher than 3600 poises
- and that it would thus be extremely difficult to prepare the spinning solution. It is preferable that the viscosity of the spinning solution be within the range of 200—2500 poises, particularly 800—1500 poises, all determined at 35° C. 70
- The above concentration and viscosity ranges, while being very important, are not absolutely critical as long as the spinning solution is "spinnable" and "stable". The former quoted term indicates that the spinning solution may be spun into fibers at a commercially acceptable rate to produce a fiber having good properties. The second quoted term indicates that the spinning solution does not gel upon standing or during the spinning operation. Thus, if the concentration of the pre-condensate is outside the above range and/or if the viscosity of the spinning solution is outside the above broad range of 40—3600 poises, it may still be possible to obtain a spinnable and stable spinning solution if other appropriate measures are taken. However, the above concentration and viscosity ranges are preferred. 75
- The pre-condensate may contain various conventional fiber additives. However, the amount of the aminotriazine-aldehyde condensation product must still be at least 60% by weight, based on the total weight of pre-condensate and any additives. 80
- The additives that may be added to the pre-condensate include other flame-retardant agents, delustering agents, pigments and any other conventional fiber additive compatible with the pre-condensate. 85
- The additives that may be added to the spinning solution include inorganic, organic and so-called "reactive" flame-retardant materials. Typical inorganic flame-retardant agents include ammonium salts such as ammonium phosphate and ammonium bromide, chlorides such as calcium chloride, zinc chloride or aluminum chloride, sodium silicate, boric acid, alums, and oxides and hydroxides of antimony and tin. Typical organic flame-retardant materials include for example, tricresyl phosphate, cresyldiphenyl phosphate, triphenyl phosphate, chlorinated paraffins and chlorinated polyphenyl. Typical "reactive" flame-retardant agents include phosphorus oxychloride, tetrakis (hydroxymethyl) phosphonium chloride (THPC) and tris-(aziridinyl) phosphine oxide (APO) etc. 90
- The fiber-forming resin [which may be either physically mixed with the aminotriazine-aldehyde condensation product per se — (i.e. the MACP) — or condensed with it as pointed out above] includes various fiber-forming thermosetting resins (other than aminotriazine-aldehyde resins) and fiber-forming thermoplastic resins. The particular resin selected will vary depending upon the desired properties of the fiber, and mixtures of resins may also be used, as well as mixtures of any 100
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- of the above additives with each other. Examples of suitable fiber-forming thermoplastic resins are thermoplastic polymers such as water-soluble polymers e.g. cellulose derivatives and polyvinylalcohol, and organic-solvent-soluble polymers e.g. polyvinyl formal, polyvinylbutyral, polyamide, polyvinyl chloride, polyethyleneterephthalate and polyacrylonitrile. The resin selected may be any thermoplastic or thermosetting resin that is fiber-forming and would be compatible with the MACP. Thermoplastic water-soluble fiber-forming polymers are preferred. Different resins are used to provide different properties to the fiber product. For example, a certain resin may be known to improve dyeability of fibers and thus may be added to the pre-condensate for the same purpose. Resins can be added for other purposes as well, as is known.
- When these resins are simply physically mixed with the MACP to form the pre-condensate, the spinning solution may be prepared by mixing an aqueous (or other solvent) pre-condensate solution with a separately-prepared aqueous (or other solvent) solution of the resin (polymer). Where the MACP is available in the form of a powder, either as a commercial product or as made by the above technique, the powdery MACP and the polymer may be separately dissolved in water (or other solvent) and both aqueous solutions then mixed together or, alternatively, the polymer may be first dissolved in water (or other solvent) and thereafter the powdery MACP may be mixed to obtain the spinning solution. The particular manner of obtaining the spinning solution is not critical, especially where mere physical mixtures are contemplated.
- In addition, the resins may be condensed with the MACP to form the pre-condensate. For example, the melamine may be condensed with the aldehyde in the presence of the resin or resins, in a solvent, to form the spinning solution. Alternatively, the condensation product may be recovered as a powder and then dissolved in a solvent (e.g., water) to form the spinning solution. Any technique can be used to form such pre-condensates.
- As pointed out above, the minimum amount of MACP in the pre-condensate is 60 weight percent, based on the total weight of pre-condensate and any additives. The spinnability of the spinning solution is improved as the amount of polymer additives (i.e., the fiber-forming resins mixed with or condensed with the MACP) increases, but on the other hand, the flame-retardant properties of the resulting fibers are decreased as the amount of polymer additive increases since these other polymers are normally inflammable. Therefore, stated conversely, from the viewpoint of flame-retardancy, the maximum amount of the polymer additives is 40 weight percent, preferably 30 weight percent, based on the total weight of pre-condensate and total additives. The minimum preferred amount of the polymer additive, particularly the water-soluble thermoplastic fiber-forming polymers, is 0.02 weight percent, based on the total weight of pre-condensate and total additives. With amounts of polymer additive below the 0.02 weight percent minimum limitation, it is difficult, though not impossible, to obtain improvements in spinnability.
- The preferred polymer additive includes a fiber-forming water-soluble thermoplastic polymer. Preferred water-soluble polymers are cellulose derivatives, polyacrylic acid, polyacrylamide, PVA, polyvinyl pyrrolidone and polyethylene oxide. Typical cellulose derivatives include carboxymethyl cellulose, methyl cellulose and ethyl cellulose. These polymers may be used alone or in the form of mixtures thereof. The preferred polymer is PVA.
- One of the reasons for incorporating such polymer additives, especially the water-soluble thermoplastic polymers, into the fiber of the present invention is to improve the flexibility and mechanical properties, such as strength and elongation, of the resulting fibers. Owing to the fact that aminotriazine-aldehyde resins are essentially hard resins and to the fact that the flexibility of a fiber consisting entirely of an aminotriazine-aldehyde resin is somewhat inferior to that of other synthetic fibers, it is preferred that the fibers produced by the process of the present invention contain at least some small amount (0.02%) of a water-soluble thermoplastic fiber-forming polymer in order that these fiber properties may be improved. Fibers of aminotriazine-aldehyde resin containing (in the case of a physical mixture) or condensed with (in the case where the polymer is actually reacted with the MACP) these water-soluble fiber-forming thermoplastic polymers have an improved flexibility and improved mechanical properties that are substantially equivalent to those of conventional synthetic fibers.
- A further reason for incorporating the water-soluble thermoplastic fiber-forming polymers in the pre-condensate and in the spinning solution of the present invention is to improve the spinnability of the latter. A spinning solution containing a resin consisting entirely of an aminotriazine-aldehyde resin is capable of being spun into a fiber by extrusion into a high-temperature atmosphere when the solution has a viscosity of 200—2500 poises. However, the spinnability of such a solution is not commercially desirable even if it has a viscosity within the stated range, since the spinning velocity is rather low (i.e., 10—20 meters per minute) and it is sometimes difficult to effect spinning at higher velocities. On the other hand, a spinning solution containing amounts of the water-soluble thermoplastic fiber-forming polymer (within the above range) exhibits an excellent spinnability at a

viscosity of 200—2500 poises and it is possible to effect spinning of such solutions at velocities of 10—150 m/min. However, it is possible to spin a fiber made entirely of an aminotriazine-aldehyde resin without the other polymer additive, although it is preferred to incorporate the latter into the former.

The spinnability of a spinning solution can be improved, as pointed out above, simply by physically mixing the polymer additive therein. A further increase in spinnability can be achieved by producing the pre-condensate in the presence of the polymer additive, particularly in the presence of the water-soluble thermoplastic fiber-forming polymer additive(s) preferably polyvinyl alcohol. For example, a spinning solution can be prepared having excellent spinnability by adding the aminotriazine to a formalin solution (which is an aqueous formaldehyde solution) of the polymer additives or, alternatively, to an aqueous solution of the polymer additives containing formaldehyde, followed by subjecting the mixture to conditions under which the pre-condensate is formed. Thus, a spinning velocity of up to about 210 meters per minute is possible utilizing a spinning solution formed by reacting an aminotriazine with formaldehyde in the presence of the polymer additives.

A further reason why it is preferred to form the pre-condensate in the presence of the polymer additive is as follows. It is theorized that the homogeneity of the spinning solution contributes to its spinnability properties (i.e., spinnability improves with increased homogeneity). Where a spinning solution is prepared by simply physically mixing the pre-condensate with the polymer additive, the resulting mixture may not be completely transparent, and this is an indication that the mixture is not completely homogeneous. On the other hand, where the spinning solution is prepared by forming the pre-condensate in the presence of the polymer additive, a homogeneous solution of the (polymer-modified) pre-condensate is obtained probably due to the fact that the aminotriazine is dispersed in the polymer solution containing the formaldehyde and the polymer and aminotriazine are both dissolved in it prior to reaction. That the resulting mixture is homogeneous is shown by the fact that the solution becomes completely transparent during reaction. The reason for obtaining a homogeneous solution in this case is not known with certainty. However, it is theorized that the reaction product solution is a mixture of (1) the (polymer additive)-modified pre-condensate, (2) the MACP and (3) the polymer additive *per se*, and it is further theorized that these ingredients are mixed homogeneously by the action of the polymer-additive-modified pre-condensate despite the fact that the MACP is not sufficiently compatible with the polymer additive. Despite the reason for it, a more homogeneous spinning

solution is obtained if the pre-condensate is formed in the presence of the polymer additive.

The solution having the best spinnability, which is preferred, is a spinning solution containing PVA, the pre-condensate and either boric acid or a borate. This spinning solution can be prepared by any one of several techniques and may comprise either a mixture of the pre-condensate and PVA with the boric acid or borate or a PVA-modified pre-condensate containing the boric acid or borate, the latter being preferred. The latter type is prepared, for example, by reacting, in solution, the aminotriazine with the aldehyde in the presence of PVA and also in the presence of the boric acid or borate.

With the former type, viz. the mixture of the PVA with the pre-condensate, several techniques are possible for preparing such spinning solutions. Thus, boric acid or the borate may be added to an aqueous solution containing the pre-condensate and the PVA. Alternatively, boric acid or the borate may be added to either or both of the pre-condensate aqueous solution and a PVA aqueous solution, followed by mixing the resulting solutions together. Another technique comprises mixing an aqueous PVA solution with an aqueous solution containing the boric acid or borate and the pre-condensate, the latter solution being obtained by reacting the aminotriazine with the aldehyde in an aqueous solution of the boric acid or borate.

A better spinnability is obtained with a PVA-modified pre-condensate rather than with a physical mixture of the two. The PVA, which may be used as an additive in this type of spinning solution, preferably has a degree of polymerization of from 500 to 3200 and a degree of saponification of 75—100 molar percent. The amount of PVA in the mixture or in the PVA-modified pre-condensate is preferably within the range of from 5 to 40% by weight, based on the total weight of the pre-condensate and PVA.

Boric acid (H_3BO_3) is preferably added to the spinning solution in an amount of from 0.2 to 20% by weight, based on the weight of PVA, and the borate is preferably added in amounts of from 0.02 to 10% by weight, based on the weight of PVA.

The borates used in the practice of the present invention may be represented by the following general formula:



wherein M represents an alkali metal atom, an alkaline earth metal atom or the ammonium ion; B is boron; O is oxygen; each of x, y, and z represents a positive integer such that $2z = vx + 3y$, where v is the valency of M; and n represents 0 or a positive integer. A typical borate that may be used in the practice of the present invention is borax (i.e.,

$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$).

The preferred spinning solution containing the pre-condensate, the PVA and the boric acid or borate can be spun at spinning velocities of as high as 500 meters per minute by extruding it through a nozzle into a high-temperature atmosphere according to the present invention. These spinning solutions also have excellent stability and good resistance against gelation or sharp changes in viscosity. Thus, a typical solution of this type does not gel or undergo sharp changes in viscosity when aged at 30° C. for periods of time longer than 10 hours. Particularly when borax is incorporated into it, the spinning solution is stable even after a period of 80 hours. Accordingly, such spinning solutions containing boric acid may be stored or aged at temperatures of from 30 to 50° C. while solutions containing borax may be kept at temperatures of 30—70° C., and yet remain stable.

With the exception of those spinning solutions containing borax, the spinning solutions of the present invention should preferably be aged or stored at temperatures lower than 40° C. This is because at temperatures above 40° C., the pre-condensate may have a tendency to further react, thereby increasing the molecular weight of the compound by cross-linking due to methylene bond formation. If this occurs, the spinning solution tends to gel and the spinnability decreases. Therefore, generally stated, the spinning solution must not be heated, prior to spinning, to a temperature that would cause further condensation of the pre-condensate with the formation of a higher molecular weight compound. Further, it is preferred to age the spinning solution, after preparation, at temperatures below 40° C. until a viscosity of 40—3600 poises, preferably 200—2500 poises and particularly 800—1500 poises (measured with a B-type rotation viscosimeter at 35° C) is achieved, if the viscosity immediately after preparation thereof is not within these ranges. However, this precaution is not essential.

In addition, the spinning solution of the present invention preferably has, a pH of from 5 to 9, and if necessary the pH of the spinning solution should be adjusted to this pH range. At pHs below 5 or above 9, the spinning solution of the present invention has a tendency to gel or undergo reductions in spinnability. However, while these undesired effects might occur at pHs outside of this range, it is not absolutely essential that the spinning solution should have this pH, although it is preferred.

In addition, the spinning solution, after being prepared, may be subjected to conventional operations normally involved in the spinning of conventional synthetic fibers. For example, the spinning solution may be subjected to a filtration and a defoaming operation.

In the reaction between the aminotriazine and the aldehyde, when an alkaline catalyst is used, or when no catalyst is employed, low-molecular-weight N-alkylool aminotriazine is obtained as a reaction product (i.e., the pre-condensate). When an acidic catalyst is used in the reaction, the same N-alkylool aminotriazine is generated, and it changes rapidly to form alkylene bonds between adjacent molecules. The pre-condensate initially formed continues, by a condensation reaction, with heating to become an insoluble and infusible three-dimensional polymer which is characterized in the present description as the aminotriazine-aldehyde resin that forms the fiber of the present invention. This is the "curing" step referred to above which is employed to produce the fiber of the present invention. Essentially, the aminotriazine-aldehyde pre-condensate is spun into filament form and subsequently cured to form the fibers of the present invention. The curing operation is performed at a temperature of 170—320° C., depending upon several factors as explained below. Depending on the spinning temperature, subsequent curing may or may not be necessary. In other words, if the spinning temperature is high enough, the curing operation occurs simultaneously with spinning. Generally stated, the only conditions necessary to cure the pre-condensate are that it be heated at a temperature and for a period of time necessary or sufficient to convert the soluble and fusible aminotriazine-aldehyde pre-condensate into an insoluble and infusible aminotriazine - aldehyde three - dimensional polymer.

Depending on the particular aminotriazine and the particular aldehyde involved in the reaction, and depending upon the presence of other co-condensable materials and other polymers, the temperature and period of time of curing will necessarily vary. However, those skilled in the art can, with a minimum amount of experimentation, determine the necessary conditions to achieve the above conversion.

Specifically, the existence of a suitable cure can be determined by the following technique. Since the cured aminotriazine-aldehyde resin forming the fiber of the present invention is not a linear polymer, it is impossible to determine the molecular weight thereof. However, the extent to which a three-dimensional infusible and insoluble network polymer is formed may be represented by the degree of cross-linking which has occurred during the curing operation, the latter which is determined from the degree of swelling (as hereinbefore defined) of the polymer. Specifically, a polymer having a low degree of swelling has a high three-dimensional network structure and, correspondingly, a polymer having a high degree of swelling (by a suitable solvent) does not have an extensive formation of a three-dimensional network structure, and can

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be said to be insufficiently cured according to the present invention.

The degree of swelling decreases with the progress of the cross-linking reaction, with the minimum of course being 1. A polymer that is not cross-linked has an infinite degree of swelling, since it would dissolve in the solvent.

- To determine the presence of a sufficient cure for the resins of the present invention, the degree of swelling of the fiber in water is lower than 2.0, preferably less than 1.5. Water is a solvent for the aminotriazine-aldehyde pre-condensate. The technique used to determine the degree of swelling in the present invention is as follows. A dry fiber having a weight of W_0 is immersed in water at 20° C for 16 hours and then dehydrated in a centrifugal separator operating at 3,000 rpm and a centrifugal acceleration of 1,000 G for 5 minutes. The resulting weight of this fiber is termed " W ", and the ratio of W/W_0 provides the degree of swelling. When the degree of swelling is higher than 2.0, the fiber has been insufficiently cured, with the result that its tensile strength and flexibility may be too small to provide a fiber having the desired properties.

Care must be taken to maintain the spinability of the spinning solution after preparation thereof. With the exception of those spinning solutions containing boric acid or borax (which may be kept at temperatures of from 30 to 70° C for periods of up to 80 hours without gellation), the spinning solutions should preferably be aged or stored at temperatures lower than 40° C, as mentioned above.

The next step in the present process, after obtaining spinning solution, and after any aging if necessary, is of course the actual spinning of the solution into fibers. Up to the present time, fibers have been prepared by either a melt-spinning process, a wet-spinning process, or a dry-spinning process. In a melt-spinning process, a molten polymer is extruded in the form of fibers and the fibers are then solidified by cooling. In a wet-spinning process, solutions of a polymer or a polymer derivative are coagulated by spinning into a coagulating bath or regenerated to form fibers. Lastly, in a dry-spinning process, a polymer solution is extruded or spun and the solvent is then evaporated to dry the fibers thereby solidifying the polymer.

Processes for preparing fibers from phenol resins (phenol resins of course being thermo-setting) are disclosed in the specifications of Japanese Patent No. 489,546 and U.K. Patent No. 1,259,829, and in Textile Research Journal, Vol. 28, p. 473. However, in these processes, a conventional melt-spinning technique is involved since the Novolak (which is a precursor of the phenol resins) is fusible by heat, and a curing reaction is effected after the fibers have been formed. Although phenol

resin fibers can be produced by a dry-spinning or wet-spinning process, the curing operation is always conducted after the formation of the fibers. It is described in the above prior art that a melt-spinning process and the curing operation can be conducted simultaneously, but in this case, heating the resin to temperatures above its melting point causes hardening of the resin, so that spinning becomes impossible within short periods of time.

Although the pre-condensate of the present invention is also molten at temperatures above 150° C., the curing of the pre-condensate into the infusible cross-linked product also occurs rapidly at such temperatures whereby the polymer becomes hardened or gelled within short periods of time. Accordingly, it is not easy to prepare the fibers of the present invention by melt-spinning, although it is possible by taking certain precautions.

Therefore, it has been realized that aminotriazine-aldehyde fibers cannot be prepared from such pre-condensates by known spinning techniques, this of course being the primary reason why the fibers of the present invention have not been known heretofore. The present invention is based on the discovery of a certain spinning technique for preparing the fibers, whereby dry-spinning of the spinning solution is conducted simultaneously with the curing of the pre-condensates. The spinning process according to the present invention is a novel process which may be termed "dry-reaction-spinning". Although the present process is analogous to a conventional dry-spinning process, since the spinning solution containing the pre-condensate is extruded into a high-temperature atmosphere (to remove the solvent), the spinning process of the present invention involves not only the drying of the solvent solution to form the fibers, but also a simultaneous curing operation whereby the low-molecular-weight pre-condensate is cured (by further condensation reactions) to form a cross-linked, polymerized aminotriazine-aldehyde resin in the form of fibers thereof. The curing operation essentially converts the fusible and soluble low-molecular-weight pre-condensate into a higher-molecular-weight infusible and insoluble polymer having a three-dimensional structure, which is mainly derived by the formation of cross-linkages due to methylene bond formation.

When the spinning solution of the present invention is merely dried to form fibers by evaporating water (i.e., a conventional dry-spinning process), the resulting product is a fibrous solid comprising a low-molecular-weight resin having a rather poor strength and flexibility thus making the winding up of the fiber very difficult or impossible. Therefore, dry spinning of the fibers of the present invention is not preferred.

The pre-condensate is cross-linked to form a high-molecular-weight polymer by the curing

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- reaction and is transformed into a colorless, transparent, flame-retardant and infusible aminotriazine-aldehyde resin fiber. Related aminotriazine-aldehyde pre-condensates have been known and have been useful mainly for molding and in adhesives and paints, and in addition have been useful for finishing fibers or papers. However, fibers composed predominantly of such resins have not been prepared because of the difficulty in devising a spinning technique for them. The present invention enables such fibers to be spun.
- The extent of the curing reaction according to the process of the present invention may be determined by the degree of water swelling of the fiber produced, determined as set forth above.
- If the spinning solution containing the pre-condensate is merely dried by evaporating the solvent thereby producing a fiber comprising a low-molecular-weight aminotriazine resin, the resulting fiber would be soluble in water and would thus exhibit an infinite degree of water swelling. On the other hand, using the dry reaction spinning of the present invention, the solvent is evaporated and the curing reaction is simultaneously effected whereby the resulting fibers are insoluble in water and have a degree of water swelling of less than 2.0. Further, as the curing reaction proceeds during spinning, the degree of water swelling approaches the minimum 1.0. However, according to the present invention, it is only necessary to perform the curing operation until the degree of water swelling is less than 2.0, preferably less than 1.5, since at values above this range, the fibers cannot be wound easily since they are insufficiently cured and have a poor tensile strength and flexibility.
- One exception is in the case of the spinning solutions which contain PVA and either boric acid or a borate. Such fibers may have a degree of water swelling of 2.0—3.0 and still may be wound up without the above difficulties. The winding is possible due to the presence of PVA in the fibers despite the fact that the curing is insufficient resulting in a degree of water swelling within the range of 2.0—3.0.
- It is preferable and desirable after the winding to further cure the fibers, such as by heating (such as by contacting the fibers with a heated roller or subjecting the fibers to a high temperature atmosphere) to obtain fibers having a degree of water swelling of less than 2.0. The temperature and the extent of time for this subsequent heating depend upon the degree of water swelling of the starting material and the degree of water swelling desired. Appropriate adjustments in the temperature and time can be made to achieve a degree of water swelling of less than 2.0.
- The dry reaction spinning technique of the present invention may be conducted as follows: The spinning solution is extruded through a nozzle into a high-temperature atmosphere (which may be air or which may be an inert atmosphere such as nitrogen) followed by winding the fibers thus formed onto a bobbin. The speed of spinning may vary from a minimum of say 10 meters per minute (where the fiber consists entirely of aminotriazine-aldehyde resin) to speeds of say 500 meters per minute (where the fiber contains same PVA). The diameter of the holes in the nozzle may vary from 0.05 to 1.0 millimeter, preferably 0.10 to 0.30 millimeter. The temperature of the atmosphere into which the spinning solution is extruded may vary from 170 to 320° C. A temperature above 170° C is required since the removal of the spinning solution solvent and the curing reaction must be effected within a short period of time to obtain cured fibers: a hardening temperature of 135—170° C is conventionally used in molding processes using aminotriazine-aldehyde resins. A temperature of above 320° C is undesirable since the resin and any other polymers present therein may be degraded at such high temperatures.
- The particular temperature selected depends upon many factors such as the speed of spinning, the resin constituting the fiber (i.e., whether the resin is solely aminotriazine-aldehyde or whether it also contains a water-soluble thermoplastic polymer such as PVA), the degree of water swelling desired, etc. For those fibers in which the resin is solely aminotriazine-aldehyde resin, a temperature within the range of 170—280° C is preferred for spinning speeds of from 10 to 20 meters per minute. Similarly, for fibers containing, in addition to the aminotriazine-aldehyde resin, other resins such as PVA, the temperature may vary from 190 to 320° C for spinning speeds approaching 500 meters per minute; the PVA may have a degree of polymerization of from 500 to 3200 and a degree of saponification of 75—100 molar per cent.
- It is not necessary to hot draw the fiber produced by the spinning process of the present invention. However, those fibers containing from 5 to 40 weight percent of a water-soluble thermoplastic fiber-forming polymer such as PVA, and having a degree of water swelling within the range of from 1.5 to 3.0, can optionally be subjected to a hot drawing operation at a temperature of above 100° C., preferably 100—200° C. The drawing operation can be conducted by contacting the fiber, under tension with a hot roller or plate heated to the above temperature or merely by passing it, under tension, through a heated atmosphere to draw the fiber at least 10% in length, i.e., to obtain a draw ratio of 1.1 times, at the minimum. The hot drawn fiber is then wound onto the bobbin. At a temperature below 100° C., it is difficult to draw the fiber more than 10% in length and since the amount of draw preferred is at least 40%,

- the temperature must be at least 100° C. In addition, with a draw less than 10%, substantial increases in the strength of the resulting fiber cannot be realized and since this is the primary purpose for the hot drawing step, the amount of draw should be at least 10%. Subsequently, the fiber is thereafter cured to obtain the desired degree of water swelling. With any fiber of the present invention, if the degree of water swelling is below 1.5, it is impossible to effect the hot drawing operation at a draw rate of at least 10%. This is undoubtedly due to the fact that, in the cured resin fibers, a cross-linked three-dimensional network has been formed. This is stable to heat and accordingly the fibers cannot be drawn easily by heating as is the case with conventional linear polymer fibers, which can be hot drawn relatively easily by heating.
- On the other hand, fibers in accordance with the present invention except that they are insufficiently cured and have a degree of water swelling of above 3.0, cannot be drawn at temperatures below 100° C. due to their lack of elongation. Further, such fibers (degree of water swelling above 3.0) cannot be drawn at temperatures above 150° C., because they have a tendency to melt and lose their fiber form: moreover, at temperatures between 100 and 150° C., the fibers can be drawn but the drawn fibers do not exhibit any increase in tenacity.
- Therefore, to summarize the optional hot-drawing step, any of the fibers of the present invention, particularly those containing the water-soluble thermoplastic fiber-forming polymer (such as 5—40% PVA), that have a degree of water swelling of from 1.5 to 3.0 before completion of the cure, may be drawn at a temperature of above 100° C. at a draw rate of above 10%. In fact, such fibers may be drawn up to about 200% (i.e., at a draw ratio of three times). Of course, the fibers must then be sufficiently cured to bring the degree of water swelling down below 2.0, preferably below 1.5.
- The tenacity of the fibers (which is generally increased by drawing) varies depending upon the degree of water swelling, the draw temperature and the draw ratio as well as the kinds and amounts of polymer additives incorporated in the fiber. The tenacity of the drawn fiber is normally within the range of from 1.7 to 5.0 g/d, which is higher than that of the undrawn fibers by 0.1—1.5 g/d.
- The size of the fiber of the present invention is of course determined by the dimensions of the nozzle used to spin it, the nozzle usually having holes of a diameter of 0.05 to 1.0 millimeter, preferably 0.10 to 0.30 millimeter.
- Generally, the fiber of the present invention has a denier of from 0.5 to 1000, although the size of the fiber of the present invention is not critical, with various sizes being preferred depending upon the particular application or end use requirement.
- In addition to having a degree of water swelling of less than 2.0, as above pointed out, the birefringence (hereinafter abbreviated as "An") of the fibers in accordance with the invention is less than 0.02. Generally, the values of An of a polymeric fiber corresponds to the degree of extent of orientation of the polymer constituting the fiber and it may generally be observed that as the drawing or stretching ratio (during the manufacture of the fiber) increases, the larger the values of An and tenacity of the fiber will become. This is because the higher the drawing ratio, the higher the degree of orientation generally. Contrary to these facts, with the fiber of the present invention, although the value of An is small, below 0.02, the fiber of the present invention has a tenacity of from 1.6 to 5.0 g/d and sufficient flexibility. In addition, the fiber of the present invention has excellent flame-retardant properties and is thermally infusible. The fiber of the present invention is especially superior compared to prior fibers with regard to the latter property, which may be clearly exhibited by the degree of shrinkage of the fiber at high temperature. The degree of shrinkage is the observed value of shrinkage, represented in percentages based on its original length, of a sample fiber 20 cm. in length after being exposed to an atmosphere of air at 300° C. for 10 minutes. Although almost all organic synthetic fibers are completely decomposed (i.e., carbonized) at 300° C., or exhibit a shrinkage of more than 50%, the aminotriazine-aldehyde resin fibers of the present invention exhibit a degree of shrinkage less than 10%, thereby indicating a superior infusibility. Unlike most organic synthetic fibers, those of the present invention as disclosed in the Examples, which follow later in this specification, in addition to exhibiting a superior infusibility, retain their original fibrous state when exposed to fire (in addition to being non-inflammable), do not gradually decompose to carbon and, in addition, generate only a very small amount of smoke when exposed to heat while maintaining a considerable part of their original strength. Considering the fact that fibers of the present invention have these advantageous properties, in addition to serving as superior flame-retardant fibers, it is thought that they will play a significant role in future flame-retardant applications.
- In addition to serving as a superior flame-retardant fiber in the formation of flame-retardant textile goods, fibers of the present invention may be used for other purposes since they have a superior whiteness and dyeability. The whiteness of the fibers of the present invention is above 0.7, as defined by Judd's formula: $W = 1 - \Delta E_{SW}/\Delta E_{BM}$, where ΔE_{SW} is the difference in color between the fiber and the standard whiteness of magnesium oxide, ΔE_{BM} is the color difference between the fiber sample and a black body

- (specific reflection therefrom being 0) and W is the whiteness value. This whiteness value is substantially the same as that of fibers made from ordinary linear polymers. With regard to the dyeability of the fibers of the present invention, the absorption of acid dye in a dye bath at 98° C. is almost 100%. In addition, the coloration is good and the dye fastness is in a range of grades 4—6 (as determined by JIS—L0843—71), which is more than sufficient for practical and general usage.
- Although the flameproof properties of fibers made from phenol resins (which, in addition to the resin of the present invention, is also a thermocuring resin) are superior, phenol resin polymers have a characteristic light-brown color. In addition, the dyeability of phenol resins is extremely poor and the appearance of a dyed phenol resin fiber is dull due to the combination of the poor dyeability and light-brown color. Therefore, such fibers are not practically useful as compared to fibers of the present invention which, in addition to their flame-retardant properties, have excellent tenacity, flexibility, whiteness and dyeability.

Fibers produced by the process of the present invention exhibit excellent flame-retardant properties such that even if they are contacted with flame, the fibers do not catch fire but instead glow only slightly and slowly. Once the flame is removed, the glowing stops almost immediately, and very small amounts of smoke are emitted during such glowing. Moreover, the fibers are thermally infusible and do not shrink substantially upon heating. In addition, fibers of the present invention have those properties required for general use. Specifically, it is relatively easy to spin and weave these fibers and products produced therefrom have a good handle since the fibers have a tenacity of from 1.6 to 5.0 g/d and a sufficient flexibility. Further, they have excellent transparency and brightness as well as an excellent dyeability, as mentioned above. The fibers further exhibit an excellent hygroscopicity of 4—11% at 20° C., 65% relative humidity, equivalent to that of cellulose fibers. In addition, fibers of the present invention have a low thermal conductivity and a sufficient resistance to chemicals, with the possible exception of acids of high concentration at high temperature. Lastly, the above properties are reduced only very slightly by washing and dry-cleaning operations.

The fibers of the present invention may be used to produce various products, such as woven fabrics, various knitted materials and of course non-woven fabrics. They may be used alone or as a mixture with other natural or synthetic fibers, as is conventional.

The present invention will be further illustrated by reference to the following examples, which are intended to be illustrative only and not limiting in any manner. In the examples,

unless otherwise noted, the term "melamine" indicates the specific compound 2,4,6-triamino-s-triazine.

EXAMPLE 1.

189 grams (1.5 moles) of melamine was added to 973 grams of formalin, having a formaldehyde concentration of 37% (i.e., 12 moles of formaldehyde) and the mixture was stirred at 85° C for 15 minutes to effect reaction. The reaction mixture was then concentrated under reduced pressure while being stirred at 60° C for three hours to obtain 920 grams of an aqueous solution of an N-methylol melamine pre-condensate. The degree of hydroxymethylation of the N-methylol melamine was 5.9. Its concentration in the solution was 49% by weight.

The solution was kept at 25° C until good spinnability was obtained, which was determined when the viscosity, measured at 35° C with a B-type rotation viscosimeter reached 260 poises. At that point, the solution was extruded through a nozzle having holes of a diameter of 0.2 millimeter into an atmosphere of nitrogen gas maintained at 250° C. The spun fiber was thus simultaneously dried and subjected to thermal curing and was then wound up to provide a fiber of 12 denier having a degree of water swelling of 1.26.

The fiber thus obtained consisted entirely of melamine-formaldehyde resin and was colorless and transparent. Its tenacity and elongation were 2.8 g/d and 14%, respectively. Its Δn value was almost 0. X-ray analysis showed that the fiber was completely amorphous. The fiber did not burn when contacted with a flame but instead only glowed slightly and slowly. The glowing stopped immediately upon removal of the flame and no smouldering was observed. The fiber was not fused by heating to 500° C and at that temperature decomposition was extremely gradual. In addition, the shrinkage of the fiber was extremely small (i.e., 3% from heating in air at 230° C. at 5% at 300° C.)

A dye adsorption of 100% was exhibited at 98° C. with an acid dye and its coloration was also excellent. The light fastness of the dyed fiber, determined according to JIS—L0843—71, was of the fifth grade. The hygroscopicity at 20° C. and 65% relative humidity was 8.6% which is sufficient for fibers used for clothing apparel. The water resistance was excellent since the fiber underwent substantially no shrinkage when immersed in water at 120° C. As for resistance to chemicals, the fiber was substantially not attacked by organic chemicals or alkalis or even acids, except for concentrated, hot acids.

EXAMPLE 2.

600 grams of a melamine-aldehyde pre-condensate having a degree of hydroxymethylation of 3.0 (Sumirez Resin 607; a product of

Sumitomo Kagaku Kogyo Company, Ltd.) was dissolved in 400 grams of dimethyl-formamide to obtain 1000 grams of a solution having a pre-condensate concentration of 60 weight percent. The solution was maintained at 30° C. until the viscosity, determined at 35° C. with a B-type rotation viscosimeter, reached 1100 poises at which point the solution was extruded through a nozzle whose holes had a diameter of 0.25 millimeter into a nitrogen gas atmosphere at 280° C. to effect the dry reaction spinning. A melamine-aldehyde resin fiber of 15 denier and having a degree of water swelling of 1.23 was obtained and was wound up at a velocity of 12 meters per minute. The flame-retardant properties were the same as the fiber of Example 1, as were the tenacity and dyeability thereof. The shrinkage of the fiber in air at 230° C. was only 3%.

EXAMPLE 3.

0.2 gram of polyethylene oxide of a molecular weight of 2,600,000 was dissolved in 140 grams of water. 259.8 g. of a melamine pre-condensate having a degree of hydroxymethylation of 3.0 (Sumirez Resin 607; a product of Sumitomo Kagaku Kogyo Co., Ltd.) was added thereto. The mixture was stirred at 160° C. for 2 hours while the pH was adjusted to 7.0 to obtain a spinning solution. The amount of polyethylene oxide in the mixture was 0.077 weight percent. The solution was kept at a temperature of 30° C. unit its viscosity, determined with a B-type rotation viscosimeter, reached 760 poises and a quite excellent spinnability was obtained. The solution was then extruded through a nozzle having four holes each of a diameter of 0.25 millimeter into air at 210° C. to effect the stable dry reaction spinning at a velocity of 40 meters per minute. The fiber thus obtained was a colorless, transparent product

having a degree of water swelling of 1.23 and a size of 9 denier. The tenacity and elongation of the fiber were 2.3 g/d and 11%, respectively. The fiber showed the same excellent flame-retardancy as in Example 1. The shrinkage of the fiber at 230° C. in air was only 2%. The fiber exhibited an excellent dyeability. Particularly, with an acid dye, a dye absorption of 100% was exhibited at 98° C. The light fastness of the dyed fiber was of the 6th grade, measured according to JIS—L0843—71. Its hygroscopicity at 20° C. and 65% RH was 6.2%, which is substantially equivalent to that of cotton. The fiber had an excellent water resistance; i.e., substantially no shrinkage in water at 120° C. was recognized. The fiber was quite stable to chemicals except acids of high concentration at a high temperature.

EXAMPLE 4.

A completely saponified polyvinyl alcohol having a degree of polymerization of 1700 was dissolved in water under stirring at 95° C. to obtain an aqueous solution. Then, Sumirez Resin 607 as used in Example 2 was dissolved therein under stirring at 60° C. for 2 hours and the pH of the solution was adjusted to 7.5. Aqueous solutions containing 0—50% by weight, based on the total weight of melamine resin and PVA, of polyvinyl alcohol were prepared. The aqueous solutions having various PVA melamine resin ratios were kept at 25° C. until viscosities of 1700—1800 poises were attained. The solutions were then extruded through a nozzle having four holes each of a diameter of 0.5 millimeter into nitrogen gas at 250° C. to effect the dry reaction spinning at a velocity of 80 meters per minute. Thus, fibers of a size of 7 denier were obtained. The results of the spinning are shown in the following table.

No.	Amount of polyvinyl alcohol (%)	Spinnability (breaking times of the fiber per hr.)	Degree of water swelling	Tenacity (g./d)	Knot strength	Flame retardancy *1
4-1	0	(Winding was impossible)	-	-	-	-
4-2	0.02	27	1.28	1.9	0.8	○
4-3	1	12	1.28	2.0	0.9	○
4-4	10	5	1.27	2.0	1.2	○
4-5	20	4	1.30	2.1	1.4	○
4-6	30	1	1.32	2.2	1.4	⊗
4-7	40	0	1.32	2.3	1.5	⊗
4-8	50	0	1.34	2.3	1.6	⊗

*1) Flame retardancy:

Non-flaming, self-extinguishing: ○

Substantially non-flaming, self-extinguishing but a considerable amount of smoke emission: ⊗

Flaming and violent smoke emission: X

The above results indicate that as the amount of polyvinyl alcohol increased, the spinnability (judged by the breaking frequency of the fiber) was improved remarkably. With no PVA, winding at 80 meters per minute was impossible. At 1%, the winding was possible to some extent. With amounts above 10%, stable winding was possible. The tenacity and knot strength of the yarn were increased by the incorporation of polyvinyl alcohol. The increase in the knot strength was particularly remarkable. Improvements in flexibility were also recognized. On the other hand, reduction in flame retardancy and emission of smoke were caused by the incorporation of combustible polyvinyl alcohol therein. Therefore, it is considered that the maximum amount of such water-insoluble polymers must be 40 weight percent, based on the total weight of melamine resin and all polymers others than melamine.

EXAMPLE 5.
12.3 grams of polyacrylamide of a molecular weight of 5,500,000 was dissolved in 478 grams of an aqueous solution of 120 grams (4 moles) of formaldehyde of pH 7.0. Then to the solution was added 126 grams (1 mole) of melamine and reaction was effected at a

temperature of 60° C. to obtain 616.3 grams of an aqueous solution of a polyacrylamide-modified melamine pre-condensate. The solution was colorless and transparent. The degree of hydroxymethylation of the melamine pre-condensate was 3.6. Accordingly, the quantity in solution of the pre-condensate containing bound polyacrylamide polymer was 246.3 grams whose concentration was 40 weight percent. The amount of the polyacrylamide polymer in the pre-condensate was 5% by weight, based on the total weight of the pre-condensate and polyacrylamide. The solution was kept at 20° C. until a viscosity of 1600 poises was obtained. The solution was then extruded through a nozzle having 7 holes, each of a diameter of 0.15 millimeter, into an atmosphere at 250° C. to effect the dry reaction spinning. The melamine resin fiber, which had a degree of water swelling of 1.20, was wound up at a velocity of 90 meters per minute. The fiber had a size of 9 denier, a tenacity of 2.6 g/d and an elongation of 13%. The fiber exhibited excellent flame retardancy, particularly little smoke emission and infusibility by heat. The dyeability and light fastness of the dyed fiber were as excellent as in Example 1.

EXAMPLE 6.

54 grams of PVA (polymerization degree: 1700 and saponification degree: 99.9%) was added to 420 grams of an aqueous solution of pH 7.0 containing 90 grams (3 moles) of formaldehyde and 2.7 grams of boric acid. The mixture was stirred at a temperature of 95° C. to obtain a solution. Then, 126 grams (1 mole) of melamine was added thereto and the hydroxymethylation reaction of melamine was effected under heating at a temperature of 60° C. for 1.5 hours. The resultant aqueous solution was completely colorless and transparent. The pH of the solution was 6.7. The degree of hydroxymethylation of the melamine pre-condensate was 2.5. Accordingly, the amount, in the solution, of the resulting pre-condensate modified with PVA was 255 grams, and the amount of the unmodified pre-condensate per se in the total pre-condensate was 79 weight percent. Therefore, the amount of PVA was 21 weight percent (based on the weight of total pre-condensate + PVA). After completion of the reaction, the concentration of the melamine pre-condensate modified with PVA in the aqueous solution was 42.5 weight percent (based on the solution). The amount of boric acid added thereto was 5 weight percent (based on PVA).

The aqueous solution was kept at a temperature of 30° C. During 10 hours, neither sharp increases in viscosity nor devitrification were recognized. When the viscosity of the solution, determined with a B-type rotation viscosimeter, was 1500 poises, the solution was subjected to dry reaction spinning. The solution was extruded through a nozzle having seven holes each of a diameter of 0.2 millimeter into air at 209° C. to simultaneously produce evaporation of water and curing of the resin. The fiber was wound up at a velocity of 260 meters per minute. The number of breaks in the fiber per hour was only two. However, when an aqueous solution containing only PVA-modified melamine pre-condensate but containing no boric acid was used as a spinning solution under the same spinning conditions, the number of breaks per hour was 74. It is therefore clear that the spinnability is remarkably improved by the incorporation of boric acid with the PVA in the spinning solution.

The fiber had a size of 4 denier and a degree of water swelling of 1.36. The tenacity and elongation percentage of the fiber were 2.8 g/d and 20%, respectively. The fiber had the same excellent flame-retardancy as in Example 1. The shrinkage at 230° C. in air was only 3%.

EXAMPLE 7.

50 grams of PVA (polymerization degree: 2400 and saponification degree: 98.5%) was dissolved in 640 grams of an aqueous solution of pH 7 containing 90 grams (3 moles) of formaldehyde and 2.5 grams of boric acid.

To the solution was then added 126 grams (1 mole) of melamine and the hydroxymethylation reaction of melamine was effected at a temperature of 50° C. for one hour. After completion of the reaction, the resultant aqueous solution of pH 7.1 was completely colorless and transparent. The degree of hydroxymethylation of the melamine pre-condensate was 2.3. Accordingly, the amount in solution of the resulting PVA-modified pre-condensate was 245 grams, which converts into a solution concentration of 30 weight percent, based on the total solution weight. The amount of the unmodified pre-condensate in the total pre-condensate was 80 weight percent and therefore the amount of PVA was 20 weight percent based on the weight of total pre-condensate and PVA. The amount of boric acid added was 5 weight percent (based on PVA).

The solution was kept at a temperature of 50° C. After a viscosity of 890 poises was attained, the solution was extruded into nitrogen at 320° C. through a nozzle having 20 holes each of a diameter of 0.10 millimeter to effect dry reaction spinning. The fiber, of a size of 2 denier, was wound up on a bobbin at a velocity of 500 meters per minute. The fiber had a degree of water swelling of 2.78. The fiber wound on the bobbin was subjected to a heat treatment in nitrogen at a temperature of 200° C. for 10 minutes to effect the curing. The fiber thus obtained had a degree of water swelling of 1.09.

The tenacity and elongation percentage of the fiber were 3.8 g/d. and 10%, respectively. The fiber thus obtained had the same excellent flame-retardancy as in Example 1. The shrinkage of the fiber at 230° C. in air was only 2%.

EXAMPLE 8.

126 grams of melamine and 112.5 grams of paraformaldehyde of 80% purity were added to 375.5 grams of an aqueous solution containing 54 grams of PVA (having a degree of polymerization of 1700 and a degree of saponification of 99.9%) and 0.40 gram of borax. Hydroxymethylation was carried out at a temperature of 80° C. for 1 hour and the degree of hydroxymethylation of the resulting pre-condensate was 2.7. Accordingly, the amount, in the solution, of PVA-modified pre-condensate was 261 grams which converts into a solution concentration of 42.5 weight percent, based on the total weight of the solution. The amount of PVA contained in the pre-condensate was 21 weight percent, based on the weight of the total pre-condensate (i.e., including the PVA modified and unmodified portions) and PVA. The amount of borax added was 0.74 weight percent, based on the weight of PVA.

The solution was maintained at a temperature of 30° C. and, during an 80-hour period,

no sharp increases in viscosity were discovered no was any devitrification observed. When a viscosity of 1800 poises was attained, the solution was extruded into air at 290° C. through a nozzle having 7 holes each of a diameter of 0.2 millimeter to effect dry reaction spinning. At winding velocity of 260 meters per minute, no breaking of the fibers occurred and in fact, the fiber was easily wound up at a velocity of 500 meters per minute. The wound fiber was then heat-treated in air to complete the cure of the resin to produce a fiber having a degree of water swelling of 1.20 and a size of 2 denier. The fiber exhibited substantially the same properties as in Example 6.

EXAMPLE 9.

50 grams of PVA (having a degree of polymerization of 2400 and a degree of saponification of 98.5%) was dissolved in 640 grams of an aqueous solution (having a pH of 7) containing 90 grams (3 moles) of formaldehyde and 2.5 grams of boric acid. To the resulting solution was then added 126 grams (1 mole) of melamine and the hydroxymethylation was conducted at a temperature of 50° C. for 1 hour. At the completion of the reaction, the pH of the solution was 7.1 and the degree of hydroxymethylation of the pre-condensate was 2.3. The amount of the PVA-modified pre-condensate in the solution was 245 grams, which is equivalent to a solution concentration of 30 weight percent, based on the total weight of the solution. The amount of the unmodified pre-condensate in the total pre-condensate was 80% and therefore the amount of PVA was 20 weight percent, based on the weight of the total pre-condensate and PVA. The amount of boric acid added was 5 weight percent based on the weight of PVA.

The solution was maintained at 50° C. and, when the viscosity of 890 poises was achieved, the solution was extruded into air at a temperature of 320° C. through a nozzle having 20 holes each of a diameter of 0.10 millimeter to effect dry reaction spinning at a velocity of 500 meters per minute. The resulting fiber had a degree of water swelling of 2.86. Subsequently, the spun fiber was contacted with heated rollers and a hot plate, both heated to a temperature of 140° C., and then wound up on a bobbin at a velocity of 1000 meters per minute, resulting in a 100% hot drawing of the fibers (due to the difference in the velocities of spinning and winding up). The wound yarn was kept in a nitrogen atmosphere at a temperature of 200° C. for 15 minutes to complete the curing reaction and produce a fiber having a degree of water swelling of 1.14 and a size of 1.5 denier.

The tenacity and elongation percentage of the resulting fiber were 5.0 g/d and 8%, respectively. The fiber had an excellent self-flame extinguishing property and was therm-

ally infusible. The shrinkage of the fiber in air at 230° C. was only 3%. In addition, the fiber exhibited an excellent dyeability, particularly with an acid dye. Specifically, a dye absorption of 100% was observed at 98° C. The light fastness of the dyed fiber was of the sixth grade and the hygroscopicity of the fiber at 20° C. and 65% relative humidity was 6.3%, making the fibers useful in clothing apparel. Further, the fiber had a high water resistance since no substantial shrinkage in water at 120° C. was observed. Lastly, the fiber was insoluble in normal solvents.

EXAMPLE 10.

An aqueous solution of N-methylol melamine having a 70% resin concentration was prepared by dissolving a commercially available N-methylol melamine (sold under the trade name Sumirez Resin 607 from Sumitomo Chemical Industrial Corporation, the resin having a degree of methylolation of 3.0) in water at 60° C. with gentle agitation for one hour. This solution was aged at 25° C. for 4 days until the viscosity thereof was 450 poises, determined as above indicated. Reaction spinning, of this solution was performed (as explained above) by spinning the solution through a nozzle into an atmosphere of air maintained at a temperature of 210° C. The holes in the nozzle had a diameter of 0.25 mm. A fiber was obtained which was 100% melamine-formaldehyde resin. Its whiteness value was 0.85, it had a denier of 16.5, a tenacity of 2.3 g/d, an elongation of 11% and a degree of swelling (in water as discussed above) of 1.22. The value of Δn was 0.002 and it was observed by x-ray analysis that the fiber was completely amorphous. After testing, it was determined that this fiber was not combustible and upon its being contacted with a flame, a gentle glowing was observed and only an extremely small amount of smoke was generated. Upon removal of the flame, the glow ceased instantly with no smouldering being observed. No tendency to fuse was observed and the fiber showed a tendency to decompose gradually only under strong heating to a temperature of 500° C. The thermal shrinkage of the fiber, at 300° C. in air, was 6% and the dyeability of the fiber was satisfactory. Specifically, the absorption of an acid dye in a dyeing bath at 98° C. was 100%. The light fastness of the fiber dyed with said dye was observed as grade 6, measured according to JIS—L0843—71.

The moisture absorption of the fiber at 20° C. and 65% relative humidity was 6.2%, a value which is near to that of cotton. On the other hand, the fiber exhibited no shrinkage when placed in hot water at 120° C. Thus, despite the fact that the fiber has a considerable ability to absorb moisture, similar to cotton, its dimensional stability in hot water is very high, this being a characteristic pro-

erty of fibers of the present invention.

EXAMPLE 11.

A mixture of 730 g of aqueous formalin, which contained 37% by weight of formaldehyde (9 moles of formaldehyde), and 189 g of melamine (1.5 moles of melamine) was reacted at 75° C. for 15 min. under stirring. After concentrating the reaction mixture by evacuation at 60° C. for 2 hrs, 835 g of an aqueous solution of N-methylol melamine of 54% concentration was obtained. The degree of methylation of the obtained N-methylol melamine was 5.4. The solution was divided equally into five receivers and they were immersed in temperature-controlled ves-

sels maintained at 20, 30, 40, 50 and 60° C., respectively. The relationship between the spinnability and stability of the solutions and the aging time were examined and the results are in Table 12 below. In the table, the spinnability is shown as the spinnable period of each solution dipped in a bath of definite temperature counted from the beginning of the dipping. The spinnability was determined by observing the fiber-forming property of each solution by dipping the tip of a glass rod in the solution and quickly drawing it up. The stability of the solutions in the table is shown as the gelation time determined when the solution lost their fluidity.

Table 12

No.	Aging Temperature °C	Spinnable Period (hr)	Gelation Time (hr)
12-1	20	15-51	60
12-2	30	11-33	40
12-3	40	4-17	21
12-4	50	1-4	4
12-5	60	-	1

Where the aging temperature was higher than 50° C., the aqueous solution of N-methylol melamine rapidly lost not only its spinnability but also its fluidity. Therefore, it is obvious that such aging conditions are improper for the present invention.

A part of the solution retained at 40° C. (No. 12-3 in Table 12) was taken out, when the viscosity of the solution, measured by a rotating viscosometer of the B-type, became 540 poises and a reaction spinning of it was carried out by spinning it through a nozzle having a diameter of 0.30 mm. into an atmosphere of air retained at 240° C. The obtained fiber had a denier of 13 and a tenacity of 2.6 g/d, an elongation of 10%, a degree of water swelling of 1.25 and a value of Δn of 0.001, and was completely amorphous. The fiber was flame retardant and infusible as in Example 10 and had a superior dyeability, especially in the case of an acid dye (i.e., C.I. Acid Red 89), which provided a dyed fiber having a clear color.

WHAT WE CLAIM IS:—

1. A flame-retardant and thermally infusible textile fiber comprising at least 60 weight percent of a cured aminotriazine-aldehyde resin and having a degree of water swelling (as hereinbefore defined) below 2.0.

2. A fiber according to Claim 1 having a

birefringence of less than 0.02.

3. A fiber according to Claim 1 or 2 having a heat shrinkage at 300° C of less than 10%.

4. A fiber according to any one of the preceding claims having a Judd's whiteness of less than 0.7.

5. A fiber according to any one of the preceding claims having a tenacity of 1.6 to 5.0 g/d.

6. A fiber according to any one of the preceding claims in which the aminotriazine-aldehyde resin comprises the condensation product of 2,4,6-triamino-s-triazine or N-substituted derivative thereof, guanamine or a substituted guanamine, or a mixture of two or more such aminotriazines, with an aldehyde capable of condensing with the aminotriazine to form a pre-condensate that is curable by heating to form a thermally infusible and insoluble polymer fiber.

7. A fiber according to Claim 6 in which aldehyde is an aliphatic, cyclic or aromatic aldehyde, or a mixture of two or more such aldehydes.

8. A fiber according to Claim 7 in which the aldehyde is formaldehyde, paraformaldehyde, dioxolane, trioxane, tetraoxane or benzaldehyde or a mixture of two or more of them.

9. A fiber according to Claim 6 in which the aminotriazine is 2,4,6-tri-amino-s-triazine

- and the aldehyde is formaldehyde.
10. A fiber according to Claim 6 in which the aminotriazine is N-butyl-2,4,6-tri-amino-s - triazine; N,N - diallyl - 2,4,6 - tri - amino-s - triazine; N - tertocetyl - 2,4,6 - tri - amino-s - triazine; N - trihalogenomethyl - 2,4,6 - tri - amino - s - triazine; or a mixture of two or more of them.
11. A fiber according to Claim 6, 7 or 8 in which the aminotriazine is guanamine.
12. A fiber according to Claim 6, 7 or 8 in which the aminotriazine is diguanamine, acetoguanamine or benzoguanamine.
13. A fiber according to any one of Claims 1 to 12 composed of 100% aminotriazine-aldehyde resin.
14. A fiber according to any one of Claims 1 to 12 consisting substantially exclusively of a cured product of condensation of an aminotriazine-aldehyde resin with a compound that is co-condensable with it, the condensation product containing at least 60% by weight of the aminotriazine-aldehyde resin, based on the weight of the condensation product.
15. A fiber according to any one of Claims 1 to 12, consisting substantially exclusively of a cured physical mixture of the aminotriazine-aldehyde resin with a second fiber-forming polymer, the mixture containing at least 60% by weight of the aminotriazine-aldehyde resin, based on the total weight of said mixture.
16. A fiber according to Claim 16 in which the second fiber-forming polymer is a thermosetting or thermoplastic resin polymer.
17. A fiber according to Claim 16 in which the second fiber-forming polymer is a water-soluble thermoplastic resin polymer.
18. A fiber according to Claim 17 in which the thermoplastic polymer is a cellulose derivative, polyacrylic acid, polyacrylamide, polyvinyl alcohol, polyvinyl pyrrolidone or polyethylene oxide.
19. A fiber according to Claim 17 or 18, in which the amount of polymer in the mixture is from 0.02 to 40% by weight, based on the weight of the mixture.
20. A fiber according to Claim 18 or 19 in which the thermoplastic polymer is polyvinyl alcohol and the amount of it present is from 5 to 40% by weight, based on the weight of the mixture.
21. A fiber according to Claim 20 in which the polyvinyl alcohol has a degree of polymerization of from 500 to 3200 and a degree of saponification of from 75 to 100 mole %.
22. A fiber according to any one of Claims 1 to 12, consisting substantially exclusively of a cured product of condensation of aminotriazine-aldehyde pre-condensate with a second fiber-forming polymer, the product of condensation containing at least 60% by weight, based on the weight of said product of condensation, of the aminotriazine-aldehyde pre-condensate.
23. A fiber according to Claim 22 in which the second fiber-forming polymer is a water-soluble thermoplastic resin polymer.
24. A fiber according to Claim 23 in which the thermoplastic polymer is a cellulose derivative, polyacrylic acid, polyacrylamide; polyvinyl alcohol, polyvinyl pyrrolidone or polyethylene oxide.
25. A fiber according to Claim 22 or 23 in which the amount of the polymer present in the product of condensation is from 0.02 to 40% by weight, based on the weight of the product of condensation.
26. A fiber according to Claim 24 or 25 in which the second fiber-forming polymer is polyvinyl alcohol and the amount of it present in the product of condensation is from 5 to 40% by weight, based on the weight of the product of condensation.
27. A fiber according to Claim 26 in which the polyvinyl alcohol has a degree of polymerization of from 500 to 3200 and a degree of saponification of from 75 to 100 mole %.
28. A fiber according to Claim 20, 21, 26 or 27, in which the fiber contains from 0.2 to 20% by weight, based on the weight of the polyvinyl alcohol, of boric acid or from 0.02 to 10% by weight, based on the weight of polyvinyl alcohol, of a borate.
29. A method of manufacturing a fiber according to Claim 1 that comprises spinning a solvent solution of an aminotriazine-aldehyde pre-condensate into a heated atmosphere to simultaneously effect evaporation of the solution solvent and curing of the pre-condensate continuously until the desired degree of water-swelling (as herein defined) is achieved.
30. A method according to Claim 29 in which the solution is spun into an atmosphere of air or an inert gas heated to a temperature of from 170 to 320° C.
31. A method according to Claim 30 in which the pre-condensate consists of an aminotriazine-aldehyde condensation product and the heated atmosphere has a temperature in the range 170 to 280° C.
32. A method according to Claim 29, 30 or 31, in which the aminotriazine-aldehyde pre-condensate comprises a fusible and soluble condensation product of 2,4,6-triamino-s-triazine, an N-substituted derivative thereof, guanamine or a substituted guanamine with an aliphatic, cyclic or aromatic aldehyde.
33. A method according to Claim 29, 30 or 32, in which the melamine-aldehyde pre-condensate comprises a mixture of (1) the condensation product of an aminotriazine and an aldehyde, and (2) less than 40% by weight, based on the weight of said mixture, of a thermoplastic water-soluble fiber-forming polymer.
34. A method according to Claim 33 in which the amount of thermoplastic polymer is not less than 0.02% by weight, based on the weight of the mixture.
35. A method according to Claim 33 or 34

- in which the thermoplastic polymer comprises polyvinyl alcohol.
36. A method according to Claim 33 or 34 in which the polymer is a water-soluble cellulose derivative, polyacrylic acid, polyacrylamide, polyvinyl pyrrolidone or polyethylene oxide.
37. A method according to Claim 29, 30 or 32 in which the aminotriazine-aldehyde pre-condensate comprises a resin obtained by condensing, in the presence of a thermoplastic water-soluble fiber-forming polymer, an aminotriazine with an aldehyde to produce an aminotriazine-aldehyde pre-condensate modified with the thermoplastic polymer.
38. A method according to Claim 37 in which the amount of thermoplastic polymer is not less than 0.02% by weight, based on the resin.
39. A method according to Claim 37 or 38 in which the thermoplastic polymer is polyvinyl alcohol.
40. A method according to Claim 37 or 38 in which the thermoplastic polymer is a water-soluble cellulose derivative, polyacrylic acid, polyacrylamide, polyvinyl pyrrolidone or polyethylene oxide.
41. A method according to Claim 35 or 39 in which the solvent solution further contains from 0.2 to 20% by weight, based on the weight of the polyvinyl alcohol, of boric acid or from 0.02 to 10% by weight, based on the weight of polyvinyl alcohol, of a borate.
42. A method according to Claim 35, 39 or 41, in which the polyvinyl alcohol has a degree of polymerization of from 500 to 3200 and a degree of saponification of from 75 to 100 mole percent.
43. A method according to any one of Claims 29 to 42, in which the viscosity of the solvent solution is from 40 to 3600 poises as measured by a B-type rotation viscosimeter, and the concentration of the pre-condensate in the solution is from 20 to 85 weight percent, based on the weight of the solution.
44. A method according to any one of
- Claims 29 to 43, in which the degree of hydroxymethylation of the pre-condensate is from 1.5 to 6.0.
45. A method according to any one of Claims 29 to 44, in which the pH of said solution is from 5 to 9.
46. A method according to any one of Claims 29 to 45, in which the solvent solution is spun into an atmosphere heated to a temperature in the range 170 to 320° C to form a melamine fiber having a degree of water swelling in the range 1.5 to 3.0 and this fiber is hot drawn at a temperature greater than 100° C and at a draw ratio of at least 1.1 times the original length of said fiber and subsequently cured by heating at a temperature and for a period of time necessary to produce a fiber having a degree of water swelling of below 1.5.
47. A method according to Claim 46 in which the pre-condensate contains from 5 to 40 weight percent, based on the weight of said pre-condensate, of polyvinyl alcohol.
48. A method according to any one of Claims 29 to 47 in which the solvent solution is an aqueous solution.
49. A method according to any one of Claims 29 to 47 in which the solvent solution is a solution in an organic solvent.
50. A method according to Claim 29, substantially as hereinbefore described with reference to any one of the Examples.
51. A fiber obtained by a method according to any one of Claims 29 to 50.
52. A fabric produced from a fiber according to any one of Claims 1 to 28 and 51.
53. A fabric composed of a fiber according to any one of Claims 1 to 28 and 51 or a mixture thereof with a natural fiber or another synthetic fiber.

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